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PREPARATION AND PROPERTIES OF SOME CYCLIC ESTERS OF PHOSPHOROUS ACID

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At the January 1946 session of the Department of Chemical Sciences, Academy of Eciences USSR, I reported on our work on the preparation and properties of the cyclic esters of phosphorous acid. In our paper (A. Ye. Arbuzov and V. M. Zoroastrova), methods were given for preparing the chlorauhydride of glycolphosphorous acid and its methyl and ethyl esters. Some of their properties and reactions were described.

We have now widened the scope of our investigations and can describe the preparation and properties of a considerable number of derivatives both of glycolphosphorous acid 'tself and of more complex compounds. We have prepared and studied the principal properties and reactions of such compounds, which can be regarded as substitution products of glycolphosphorous acid and, consequently, of orglycels, forming a five-member ring with an atom of phosphorus.

We shall further describe the preparation and properties of a small number of cyclic derivatives of phosphorous acid, such as the derivatives of β -, γ -, and δ - glycols, which form the corresponding six-, seven-, and eightmerber rings with a phosphorous atom. The tertiary valency of phosphorus is absorbed by the chlorine atom and the alkoxyl group, and thus we shall acquaint the meeting with chloranaydrides and compound esters of alkoxy- α , β -, γ -, and δ -glycolphosphorous acids.

To depict the fairly complicated picture of the properties and transformations of the compounds studied as fully as possible, I append some properties and transformations of compounds described previously.

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First, I shall consider the preparation of the chloraphydrides of various glycolphosphorous acids synthesized.

The following glycols were used as initial compounds: (1) ethylene glycol, (2) Of-methoxypropylene glycol (the Of-methyl ester of glycerol), (3) 1,3-butylene glycol, (4) 1,4-butylene glycol, ani (5) diethylene glycol (See Table 1).

Table 1

Ė	Nd	Formula		20	20		
			tp (in °C)	₹ <mark>5</mark> 0	uĐ Sọ	MR _D Experi- mental	MR _D Calculated
	1.	CH ₂ - 0 PC1 CH ₂ - 0	41.5/10 mm	1.4172	1.4915	25.46	25 .5 8
	2	сн ₃ 0 — сн ₂					
		CH ₂ O PC1	78.5 - 79.2/9 ==	1.2984	1,4722	36.77	36.46
†	3	CH ₂ - CH - O	65/12 mm	1.2496	1.4765	34.91	34.81
	14	CH ₂ - CH ₂ - O FC1	74-75.5/8 mm	1.285%	1,5010	35.33	34.81
	5	OCH2 - CH2 - OPCI	104-105/15 mm	1.2693	1.5165	40.14	39.43

The chloranhydrides were prepared by the action of phosphorous trichloride on the glycol, awaity in a solution of dry ather in the presence of pyridine (r. r. Milobend-skiy) or dimethylaniline (m. Ye. Arbuzov and K. V. Nikonarov). On completion of the reaction, the aniline hydrochloride was removed by means of a Nutsch filter, the ether was evaporated and the residue fractionated, usually from an Arbuzov flags. Yields were satisfactory for α - and β - glycols but considerably poorer for β -, γ -, and δ - glycols γ - and γ - glycols.

The chlorar hydrides of α -glycels are colorless liquids which fuse in air. They are excendingly active and in this respect are reminiscent of the chlorar hydrides of dralkylphe-phorous acids, capacially those of ethylphe-phorous acids,

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The yield of the chlorathydride of 1,3-butylene glycol is excellent, and the compound is relatively stable. Evidently, the six-member ring is more stable than the five-member o.s. On the other hand, the yield of the chlorathydrides of 1,4-butylene and diethylene glycols is very small and extremely unstable. It tumes vigorously in air and immediately catches fire and burns with a blue flame when poured on to a filter paper.

In the pure state, the seven- and eight-member chloranhydrides are colorless, mobile liquids. However, even in closed receptacles they polymerize rapidly into a colorless, gelatinous mass which later turns yellow, evidently due to the evolution of red phosphorus.

The chloranhydrides can be used as initial compounds for preparing the full compound esters of phosphorous acid by the action of anhydrous alcohols in the presence of pyridine or dimethylaniline.

However, the method we generally adopted when preparing compound alkyland aryl-cyclic esters of phosphorous acid was to start from Menshutkin's chloranhydrides and the corresponding glycols.

I shall now acquaint the reader with the compound esters of the various glycolphosphorous acids prepared. We synthesized 14 esters, only one of which contains the aromatic phenyl radical.

Table 2

No	Formula	(in °C)	⁴ 0	ng 20	MRn Experi- mental	MRD Calcu- lated
1	$ \begin{array}{c c} CH_2 & - O \\ I & \\ CH_2 & - O \end{array} $ $P - OCH_3$	55-56/23 mm	1.2159	1.4460	26.77	26.96
2	CH ₂ - 0 P - 0C ₂ H ₅ CH ₂ - 0	51.5-51/15 mm	1.1317	1.4395	31.66	31.62
3	CH ₂ - 0 P - OC ₄ H ₂ (n) CH ₂ - 0	71-72 / 8.5 mm	1.0819	1.4470	40.53	40.87
4	CH2 - CP P - OCH2CH2C1	78.979. 5 /6.5 nm	1.3206	1.4755	36.39	36.46
5	ся ³ о - ся ⁵	77-78/9 ====	1.1793	1.4459	37.52	37.85
6	CH ₃ O - CH ₂ CH - OP - OC ₂ E,	84-85/10 mm	1.1415	1.4498	42.39	42.44

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Ta	ble 2 (Contd)			and the second		po (**x;
7	СН ₃ 0 - СН ₂ СН - О СН ₂ - ОС _Ц П ₉ п	ىسى 9/9-107-107	1.0713	1.4450	51.73	51.71
8	CH ₃ 0 - CH 3 CH - 0 P - 0C ₆ H ₅	145,5-106/7 mn	1.2130	1,4768	53.11	52.14
9	C ₂ H ₅ O - CE ₂ CH - Q CH ₂ - OC ₂ H ₅	93-94/7 mm	1.0937	1.4401	46.6 8	47.08
10	CH - CH ₂ CH - O P - CC _{li} H ₉ (n)	108.5-110/8 mm	1.1629	1.4601	50.07	50.41
11	CH ₂ - O CH - O CH - O	62/13 mm	1.1092	1.4420	35.80	36.20
12	CH ₂ - O CH ₃ CH - O CH ₃	63-64/8 mar	1.0695	1.4410	40.51	40.31
13	CH ₂ - CH ₂ - O CH ₂ - CH ₂ - O P - OCH ₃	54-55/4.5-5 mm	1.1649	1.4642	35.60	36,20
14	CH ₂ - CH ₂ - O P - CC ₁ H ₂ (n	100-102/9-10 mm	1.0557	1.4540	49.28	50.05

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The physical and chemical properties of the estera synthesized depend to a considerable extent on particle size and structure. In general, they are very active commonnds. The compounds of low molecular weight recall the methyl or ethyl esters of passing our sold, in regard to both oder and oxidation tendencies. Many of them oxidize with flame under the influence of strong nitric acid, similar to trimethyl phosphite.

An energetic reaction with water accompanied by the evolution of a large amount of heat is typical of all these esters. Many of them, being trivalent phosphorous derivatives, yield compounds with the monohalide salts of copper (A. Ye. Arbuzov's reagent). Some of these were obtained in the crystalline state.

Table 3

	rante 2	
No	Formula	mp OC
1	CH ₂ - 0 POCH ₃ . CuJ	135 - 133
5	CH ₂ - 0 POC ₂ H ₅ . CuJ	
3	CH ₂ - 0 FOC ₂ H ₅ . CnJ	135
14	CH ₂ - CH ₂ - O POCH ₃ . CuJ	142 - 144

For the same reason, sulfur addition compounds were obtained for some of the esters synthesized. Sulfur unites very energetically with methyl ester α -methoxymetrylglycol ester of phosphorous acid. When one gram of sulfur combines with 5 grams of ester, the temperature rises from 20° to 105° .

On the other hand, addition of sulfur to the analogous ethyl ester proceeds sluggishly and requires heating to 110° - 120° .

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Table 4

		Elekarian di Laborat di	Company of the Arrest of
No	Formula	bp (in ^{SU})	D 0 n p
1	CH ₂ - 0	117 -112.5/1.5 mm	1.2877 1.4889
2	CH ₂ - O P - CC ₂ H ₅	121.5-122/2	1.2359 1.4790

All the foregoing properties and reactions of the 14 cyclic compound esters of phosphorous acid synthesized are in general very reminiscent of the properties of the full alkyl esters of phosphorous acid and especially of those of trimethylphosphite.

I now pass to a more interesting part of my paper -- the examination of the reactions of the cyclic esters where the effect of their structure is most pronounced.

This effect is manifested when they are subjected to the action of alkyl halides, e.g., benzoyi chloride or bromide, triphenylmethane bromide, to the action of water, to the action of acyl halides, e.g., acetyl bromide, chlorocarbonic ester, etc.

It is interesting to note that all the cyclic esters studied fall into two groups with respect to the reagents enumerated. In the first group, as a rule, the reaction is accompanied by opening of the ring. In the second group the ring system remains intact. As will be seen later, there are also cases where the ring is broken under the influence of one reagent and is retained under that of another.

Yet another enlargement of the foregoing statements is the fact that we did not observe a single case where a cyclic ester reaction (e.g., with an alky halide) proceeded simultaneously along both lines, i. e., with and without rung opening. However, we cannot assert that such cases do not take place, if only because the yield of the final products is usually small and consequently the fate of a substantial proportion of the initial compounds is unknown.

In my paper at the January 1945 session I reported on some properties of mixed alkyl-cyclic esters of phosphorous acid synthesized from ethylene glycol. It was possible to consider the easy opening of the five-member heterocyclic ring formed by two carbon atoms, two oxygen atoms, and the phosphorous atom as the most typical and unappected property of these suterc. This is confirmed by Table 5.

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Table 5

No	Formula	bp (1n °C)	20	² 50
1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	129-130/11 mm	.,3726	1.4610
S	$\begin{array}{cccccccccccccccccccccccccccccccccccc$.82-183/7.5-8 nm		1.5128
3	$CH_{2} = 0$ $CH_{2} = 0$ $CH_{2} = 0$ $CH_{2}Br + CH_{2}OF - CCH_{3}$ $C(C_{6}H_{5})_{3}CF + CF_{2}OF + CF_{3}CF + CF_{$	M. P. °C 153-155		
4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	99-101		

It would nowever, be premature and venturesome to conclude, on the basis of a study of the properties of the alkylethylene glycol esters of phosphorous acid, that other alkyle &-glycol esters will also be characterized by ease of opening of the five-member ring.

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It would seem that in our further study of the alkyl cyclic esters of phosphorous acid we should have synthesized the alkylpropylene glycol esters. But at that time we had no propylene glycol at our disposal and therefore continued to work with glycerine: Having obtained methyl-substitution glycerine in A-hydroxyl, we thus had, as it were, methoxy-substitution propylen glycol. Proceeding from this compound, as can be seen from Table 2, the mixed methyl, ethyl, n-butyl and phenyl esters were synthesized.

Similarly, proceeding from glycerine, we prepared α -ethoxypropylene glycol and α -monochlorhydrin glycerine, otherwise known as α -chlorpropylene glycol.

Working from these compounds, we synthesized two more esters -- the ethyl ester of ethoxypropyleneglycolphosphorous acid and the n-butyl ester of α -chlorpropyleneglycolphosphorous acid.

In no case did any of these six esters containing the five-member ring display a tendency to ring cleavage when acted on by the same reagents, in contrast to the alkylethyleneglycol esters, as can be seen from Table 6.

Table 6

	rapte o	gwy Mei yn de Grife.	1.
No	Formula	bp (in °C)	mp °C
1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	140-141/3 mm	
Si	CH ₃ O - CH ₂		88-89
3	CH ₂ O - CH ₂ CH - O CH ₂ - OC ₂ H ₅ + C ₆ H ₅ CH ₂ B: → CH ₂ C ₆ H ₅ CH ₂ - OC ₂ H ₅ + C ₆ H ₅ CH ₂ B: → CH ₂ C ₆ H ₅		88-89
14	CH ₂ O - CH ₂ CH - O CH ₂ - OC ₂ H ₅ + C ₆ H ₅ CH ₂ CH ₂ CH CH ₂ OCH ₂ OCH ₂ CH ₂ OCH ₂ OC		88-89
5	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	198-199/2 m m	
6	C1 - CH ₂ CH - O CH ₂ - CP ₄ + CH CH Br → CH ₂ - O CH ₂ - O CH ₂ C6H ₅		94-95

Thus, displacement of one hydrogen atom for various radicals in the alkylethylene glycol esters of phosphorous acid does not break the ring, as might have been thought, but stabilizes it.

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Let us consider the mechanics of all transformations of the cyalic esters studied.

Despite the seeming distinction between ring cleavage and non-ring cleavage ester reactions, their mechanism is the same, and is that of the trialkyl phosphite transformations, as consequences be seen from the following scheme:

$$\begin{array}{c} C_2 H_5 O \\ P \longrightarrow C_2 H_5 + C_2 H_5 Br \longrightarrow C_2 H_5 O \\ C_2 H_5 O \end{array} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H_5 O \\ C_2 H_5 O \end{array}} \xrightarrow{\begin{array}{c} C_2 H$$

I shall now examine the action of water on some of the cyclic phosphorous esters synthesized. Water acts in different ways on trialkyl phosphites. It acts extremely energetically on trimethyl phosphite, especially in the presence of the smallest traces of hydrogen ions. On the other hand, triethyl phosphite can be heated in pure water over 100° for a long time without any noticeable alteration.

All the cyclic esters with a five-member ring studied react very readily with water, with evolution of a large quantity of heat, but as in the other cases discussed, the reaction proceeds along two lines -- with or without ring cleavage.

We studied the action of water on six esters.

As was pointed out in our previous paper, water reacts vigorously with the ethyl ester of ethyleneglycolphosphorous acid with ring cleavage. The action of water on the ring-substitution enters of ethyleneglycolphosphorous acid proceeds just as vigorously, but the ring is preserved with the evolution of the corresponding alcohols in the free state. Moreover, the action of water on the phenyl ester of of methoxylpropyleneglycolphosphorous acid also proceeds with preservation of the ring and evolution of phenol.

All that I have expounded is clearly visible in Table 7.

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bp 142-143°/11 was - CH201 1.4825 CH⁵ CH2OHCH2OF + нон bp 156-1580/10 mm CH 30CH 5 CH 1.4719 CH2-CE3OCH 2 CH -Œ2bp 144-145°/2 mm C1CH2 n_D20 1.4898 CH POCh H9 + 110H -ĊН2bp 127-129°/2.5 mm с₂в5 1.4588 oc₂H₅ + HOH →

The hydrolysis products of all the esters studied are colorless, viscous, odorless liquids which evaporate in vacuo without decomposing at high temperatures. Due to the consistency of these compounds, it was not possible to determine their specific gravity. We tried to prepare metallic derivatives of these original acids, but have not as yet succeeded.

Compounds with six-member, and, especially, seven- and eight-member rings have not been studied so thoroughly.

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As can be seen from Table 2, we synthesized the methyl and ethyl esters of 1,3-butyleneglycolphosphorous acids. These esters have the least yields.

In regard to their reactions to various reagents, as yet we have studied only the action of trimethylene bromide on the methyl and ethyl esters of 1,3-butyleneglycolphosphorous acid.

The reaction took place in the presence of small quantities of dry benzene during heating of the mixture to the boiling point of benzene for half an hour.

The reaction proceeds without ring cleavage, the corresponding bromide being formed -- methyl bromide in the first case and ethyl in the second.

The reaction product is the same in each case -- 1,3-butyleneglycol.

The esters of triphenylmethylphosphorous acid are crystals with melting point
192-193 degrees. As can be seen, the ring is preserved during the reaction.

I shall say a few words on derivatives containing a seven- and eight-member ring.

We did not attempt to prepare these esters from the chloranhydrides synthesized from 1,4-butylene glycol (tetramethyleneglycol) and diethylene glycol in view of the already-mentioned instability of these chloranhydrides.

We prepared the ester with a seven-member ring from Menshutkin's chloranhydrides, acting on them with 1,4-butylene glycol in the presence of pyridine. These esters, like the chloranhydride, are very unstable and began to deposit crystalline products while their specific gravity was being determined. No derivatives have as yet been obtained.

A mixed ester of phosphorous acid with an eight-member ring could not be prepared. However, we have not lost hope of preparing these capricious and unstable compounds for future study of their properties and reactions.

In connection with the action of acetyl bromide, chlorocarbonic ester, and carbon tetrachloride on some of the esters prepared, we studied the action of acetyl bromide on the methyl and acetyl esters of methoxypropylenephosphorous acid. The action of acetyl bromide on the methyl ester is extremely energetic, and a considerable amount of heat is evolved. The ring remains intact. The acetylene derivative of methoxypropyleneglycolphosphorous acid is a mobile liquid with boiling point 141-142.5° at p = 2 mm.





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The reaction of acetyl bromide with the ethyl ester is somewhat less energetic and, surprisingly, is accompanied by ring cleavage. The compound obtained is a liquid with boiling point, $13f-132^\circ$ at p=2 mm. It is noteworthy that the boiling point of this compound is low in comparison to that of the reaction product, methyl ester, although the molecular weight of the compound containing a browine atom is considerably higher.

The reaction of the chlorocarbonic ester with the ethyl ester of methoxypropylenephosphorous acid also leads to ring opening. The reaction product is a liquid whose boiling point is $144.5^{\circ}-146^{\circ}$ at p = 1.5 ma; n_{D}^{20} 1.4520.

I shall also mention a reaction of carbon tetrachloride on the ethyl ester of methoxypropylenophosphorous acid which we succeeded in bringing about only once. The reaction takes place in a sealed tube on heating to $160^{\circ}-170^{\circ}$ for almost 24 hours. The reaction product is a viscous liquid whose boiling point is $144^{\circ}-150^{\circ}$ at p = 1.5 mm. After evaporation the liquid crystallized into a solid mass. Analysis showed that the ring was preserved and ethyl chloride evolved. The substance obtained is unstable and its properties could not be studied in detail. Seven attempts to repeat the experiment were unsuccessful, decomposition occurring at the commencement of evaporation.

In conclusion, all the structural formulas given in the tables are, in our opinion, the most probable but have not yet been rigorously proved.

While performing the experiments and writing this article we were unavoidably ignorant of M. I. Kabachnik and P. O. Rossiyskaya's article on the same subject, "A Study of the Reaction of Glycols with Phosphorous Trichloride and Menshutkin's Chloranhydride" ("Izv Ak Nauk SSSR, Otdel Khim Nauk" No 5, 1947, p 509).

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